Tannin: impacts and opportunities along the value chain

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Studying tannins is challenging. Their behaviour is rarely predictable; results can be contradictory and experiments often seem to generate just as many questions as they answer. But if you step back and take a broader view of the tannin research conducted over the past few years, you can see that real progress has been made in understanding tannin at key points across the grape and wine value chain, with practical outcomes for growers and winemakers.

AT A GLANCE

Recent tannin research has delivered:

- Simple measurement of tannin and colour in grapes and wine
- Breakthroughs in understanding the extraction of grape tannin during fermentation
- Knowledge of the influence of grape maturity on eventual wine colour and tannin
- Practical winemaking techniques that can be used to manipulate tannin
- New understanding of what happens to tannin as wine ages and the importance of tannin structure for sensory properties
- Insights into factors influencing colour stability

FROM GRAPE TANNIN TO WINE TANNIN

Wine tannin originates from the tannin present in grapes; however, the journey from grape tannin to wine tannin is not a straightforward one. Grape tannin needs to be extracted from solid grape material into must during fermentation, and then undergoes chemical rearrangements to reach its final wine tannin form. This is why it is not a simple task to predict eventual wine tannin by measuring grape tannin – something winemakers would like to be able to do.

Understanding extractability

The extractablity step in the process – getting the tannins out of the grape solid material and into must – has been investigated, with a focus on the role played by grape cell walls (AWRI publications #1181, #1236, #1280 and #1458).

A number of factors were discovered that influence how easily tannin is extracted:

- skin and seed tannins were found to interact with grape cell wall material and this interaction limited the amount of tannin extracted during fermentation
- cell wall material interacted more strongly with seed tannin than skin tannin, most likely due to differences in their structure
- suspended flesh (pulp) material was shown to bind and remove tannin as lees during settling after the tannin had been extracted during fermentation
- grapes with a low overall tannin concentration and grapes with a higher seed-to-skin tannin ratio were more affected by this removal of tannin by pulp
- seed tannin was shown to be less extractable than skin tannin during fermentation, but this varied significantly between seasons.

Influence of grape maturity

The effects of grape ripening on factors affecting extractability were also investigated (Bindon *et al.* 2013a). Riper grapes were associated with:

- increased total skin tannin concentration which could lead to higher wine tannin
- higher cell wall porosity which can result in a greater amount of total skin tannin trapped in the pores
- higher anthocyanin, which appears to enable the extraction of tannin
- higher sugars leading to higher ethanol levels, which may increase tannin and colour extraction.

Results from these studies of extractability have highlighted the role of cell wall material in influencing tannin concentration during fermentation. The new understanding gained could lead to the development of methods to predict the extractability of tannin for a particular batch of grapes.

WINEMAKING

Influence of oxygen on wine tannin and colour

As soon as grapes are crushed, chemical reactions start taking place that continue through fermentation and ageing and eventually determine the wine's final colour and taste. One key example is the reactions that convert grape tannins into more complex wine tannins. Oxygen has long been known to modify the astringency of red wines, but the chemical basis of this observation was unclear. Winemaking experiments were conducted to investigate what happened when air was injected into red wine fermentations. Results showed important effects of air additions on tannin concentration and chemical structure, with accompanying sensory effects. In particular, air reduced the concentration and size of tannins, increased stable colour formation and reduced the astringency of the wines compared with the wines not treated with air (Day *et al.* 2013). This new knowledge provides practical options for winemakers to influence tannins during fermentation.

Impact of novel yeasts on tannins to improve wine quality

Yeasts are well known to influence wine aroma but their effect on macromolecules and texture has been less well explored. A selection of yeasts were investigated for their effects on colour and tannin and were shown to influence final tannin concentration by up to 50%, and to also significantly affect wine colour (Blazquez Rojas *et al.* 2012). Further studies that evaluated the effects of fermenting Shiraz and Pinot Noir (AWRI publications #1542 and #1562) with different yeast strains again showed a strong influence of yeast strain on tannin concentration. As an example, in experiments with Shiraz and Cabernet Sauvignon, wines made with *S. bayanus* strain 1375 and *S. bayanus* AWRI 1176 had consistently low tannin but the tannin was highly pigmented, while wines made with *S. cerevisiae* AWRI 1486 had generally high tannin and the tannin was highly pigmented. This work demonstrates that the colour and texture of red wines can be significantly modulated by choice of commercially-available wine yeast.

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Tannin measurement now widely available

In the past, lack of accessibility of methods to measure tannin has been a barrier for winemakers in optimising wine tannin and colour. Development of the simplified methlycellulose precipitation (MCP) tannin assay was the first step in breaking down that barrier. This method is now published in the widely used 'Chemical analysis of grapes and wine; techniques and concepts' handbook by Iland *et al.* (2013), along with data from the Australian

wine tannin survey that communicates what can be considered low, medium and high tannin concentrations. An even simpler option is the web-based tool offered by the AWRI that allows producers to measure and benchmark tannin and colour in both grapes and wine. This tool forms a component of the WineCloud™.

Investigation of compounds with sensory impact

The importance of the structure of red wine tannin in influencing wine mouthfeel has been investigated (AWRI publication #1504). The study showed that larger and more water-soluble wine tannins are more astringent, while smaller wine tannins that are less water-soluble, more coloured and have more oxidative structures, were perceived as hotter, more bitter and less astringent. These results demonstrate that different types of tannins can influence mouthfeel and confirmed that modifying wine tannin structures during winemaking is a practical path to altering the wine mouthfeel.

AGEING

Colour development and stability

During red wine ageing, winemakers hope for the formation of long-term, stable, red colour. Yet in some situations, colour is inadequate from the beginning or is unstable and fades fast. While some of the factors influencing stable colour formation are known, others remain a mystery. One of the main reasons for the colour change seen in wine during ageing is the decrease in anthocyanins (red pigments derived from grapes), as well as changes to pigmented tannins (stable coloured compounds formed by reactions between anthocyanins and tannins). Analysis of 30 and 50 year vertical series of Cabernet Sauvignon and Shiraz wines showed that wine colour density was more strongly associated with pigmented tannins over the 30 and 50 year series than with anthocyanins (after the first two years post-bottling), clearly reinforcing the importance of pigmented tannins to wine colour. In general, by four years no coloured anthocyanins were left in red wine (AWRI publication #1488).

In a separate experiment, wine colour density was tracked through three years of ageing in wines of both high phenolic potential (high anthocyanin, high tannin), and low phenolic potential (low anthocyanin, low tannin) (Bindon *et al.* 2013b). Higher wine tannin and anthocyanin led to enhanced wine colour density and stable non-bleachable pigments, which were retained through ageing. Formation of non-bleachable pigments was found not to increase beyond two years of ageing. The incorporation of colour with ageing was proportional to tannin concentration. Non-bleachable pigments were formed via multiple routes, such that high-tannin, high-anthocyanin wines formed greater quantities of both polymeric and non-polymeric red pigments. Further work is required to understand how these alternative mechanisms for stable pigment formation can be harnessed. To summarise, low tannin concentration doesn't necessarily prevent the formation of stable non-bleachable pigments, but high tannin concentration maximises the likelihood of long-term colour stability.

Astringency changes

Analysis of the vertical series also clearly indicated that aged red wines can have similar tannin concentrations to young wines, dispelling the commonly held belief that changes in red wine astringency with ageing are due to the loss of wine tannins through precipitation. Such changes in astringency are instead due to compositional changes in tannins, although the rate of these changes is unknown.

The structure of tannins isolated from older wines were analysed to try to understand the changes observed in astringency as wines age (AWRI publication #1255). The 'aged wine tannins' were shown to only weakly associate with saliva-like proteins compared with tannins from younger wines. This is consistent with observed lower astringency of old wines, as the sensation of astringency is linked with strong associations between tannins and salivary proteins. In addition, the analysis revealed a large proportion of tannin that cannot be broken apart (i.e., tannin that is non-hydrolysable), unlike grape tannin that is readily broken apart. This non-hydrolysable proportion of wine tannin has also been shown to have a very weak association with saliva-like proteins and accounts for a larger proportion of aged wine tannins than young wine tannins. These results may, at least in part, explain why red wines 'soften' with age.

An additional experiment demonstrated that tannin structure in Shiraz wines is not influenced by storage at different pH levels (3.2, 3.5 and 3.8) or under different screwcap closures with specific oxygen transfer rates after two years of bottle ageing, even though wines of lower pH are often reported as more astringent (AWRI publication #1571). This suggests that a lower pH has a direct effect on the sensory perception of the wine examined, but doesn't necessarily influence wine tannin evolution. These results provide improved insight into the stability of tannins in wine and underscore the importance of wine matrix influences on perceived mouthfeel.

Overall, astringency has been demonstrated to depend on the type of tannin and not just the amount present. In the future by targeting the creation and retention of specific types of tannins, it should be possible to create wines that have the softer mouthfeel of an aged wine, but at a much younger age.

A higher tannin content doesn't always result in a higher consumer liking.

CONSUMER

Higher tannin doesn't always mean higher consumer liking

A major trial was conducted in which Cabernet Sauvignon wines were produced from grapes from the same vineyard harvested at five different maturity stages. The wines were found to have significant differences in tannin and colour, with lower alcohol (12%) wines having lower tannin, a lower proportion of skin-to-seed tannin, and lower colour and polymeric pigment compared with higher-alcohol wines (15%) (AWRI publication #1507). Astringency increases were correlated with higher tannin for later-harvested wines (Bindon *et al.* 2013d). As part of the experiment, the five wines were presented to a group of consumers who rated how much they liked the different wines. Results showed that wines of 13% alcohol or higher were preferred compared with the lower alcohol wines. However, no further increases in consumer liking were observed for the wines between 13% and 15% alcohol, despite increases in tannin (Bindon *et al.* 2013d).

Importance of tannin structure on wine quality

There continues to be demand from industry for understanding how wine tannin composition (not just concentration) influences quality, wine grading or price, and research has addressed the role of tannins in the quality/grading/price nexus (AWRI publication #1188). Quality (defined as winemaker-assessed allocation gradings that ultimately relate to market price) in young red wine was positively correlated with tannin concentration, tannin size, higher proportion of skin-derived tannins and overall wine colour (AWRI publications #1254 and #1323). This suggests that maximising skin tannin concentrations and/or proportions in wines can contribute to an increase in projected wine bottle price, but this must be done in balance with the other wine components that contribute to the desired wine style. The management factors associated with increased skin tannin concentrations include:

- reduced vine vigour and vine water status
- increased fruit exposure
- increased berry crushing prior to fermentation, combined with reduced soak time
- use of enzymes.

CONCLUSIONS

Effectively managing vineyards and winemaking to optimise grape and wine tannin and colour translates into increased capacity for the Australian wine industry to meet wine specification, consumer expectations and profitability. Specific areas where winemakers can now take practical steps to influence wine tannin include:

- choice of yeast
- management of oxygen during fermentation
- viticultural and winemaking choices that aim to optimise proportions of skin tannin.

Tannin research at the AWRI has provided the Australian wine industry with an improved understanding of structures, measurement, formation and function of phenolics compounds responsible for wine texture and colour, and has significantly progressed the scientific framework for improvements in winemaking. It has identified several areas with potential to return high value and knowledge gaps for future research. In particular, the importance of understanding how tannins, proteins and polysaccharides work together in wine represents a research opportunity with significant potential to support the production of desired wine styles. This work is continuing in Project 3.1.4 of the AWRI's R,D&E plan 2013-2018.

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